

STUDIES OF MANY-BODY EFFECTS
IN X-RAY SPECTROSCOPY OF SOLIDS

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1974

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by

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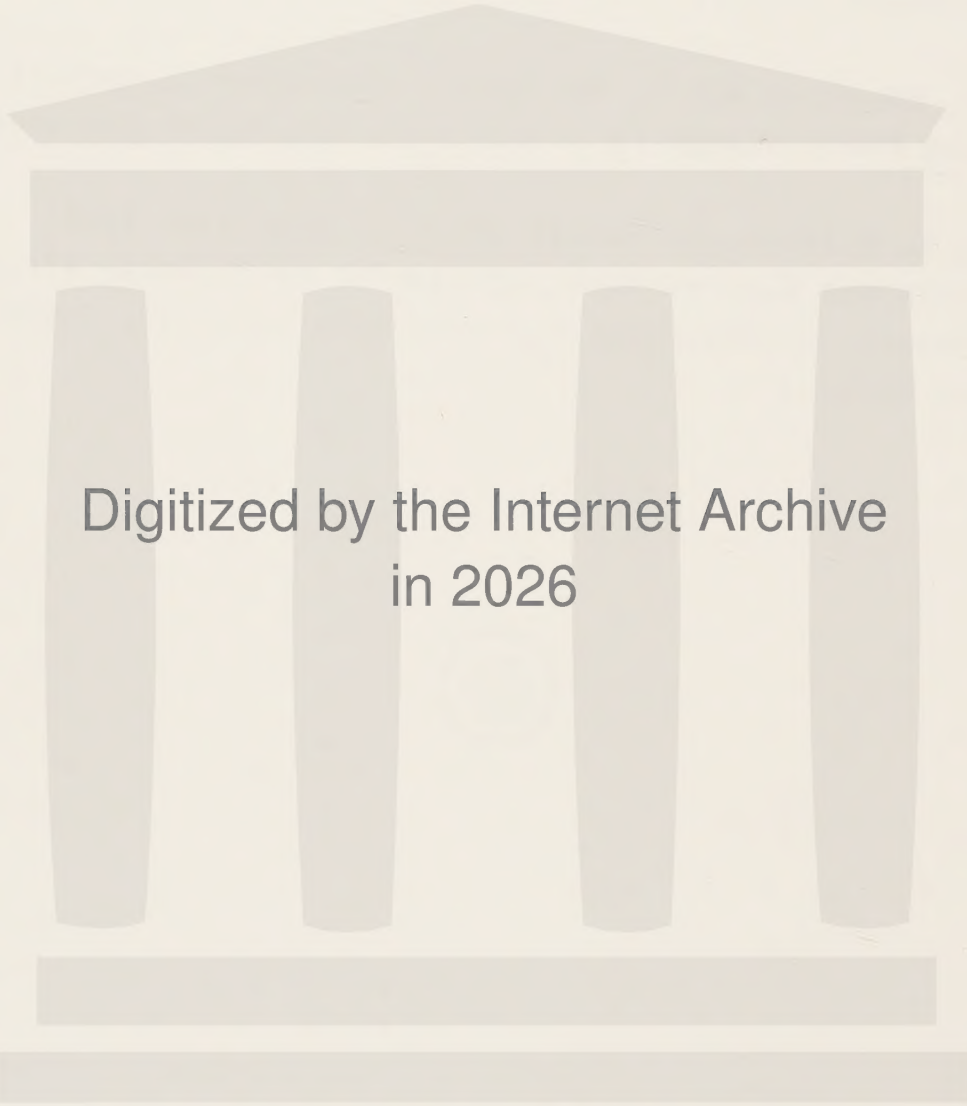
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LÄGGES TILL OFFENTLIG DISPUTATION FREDAGEN
DEN 29 NOVEMBER 1974 KL 10.15 I FÖRELÄSNINGS-
SALEN VID INSTITUTIONEN FÖR TEORETISK FYSIK,
LUNDS UNIVERSITET



The present Paper is an introduction to and a summary of a thesis comprising the following four papers:

- A. C.O. Almbladh: Incomplete Relaxation in a Model Problem for the Auger Process, *Il Nuovo Cimento* 23 B, 75 (1974)
- B. C.O. Almbladh and U. von Barth: The Spherical Solid Model: An Application to the X-ray Edges of Li, Na and Al, to be published
- C. C.O. Almbladh and U. von Barth: Non-Linear Screening of a Fixed Point Charge in an Electron Gas, to be published
- D. D.J.W. Geldart, M. Rasolt and C.O. Almbladh: Self-Consistent Hartree-Fock Calculation of Exchange Effects in a Weakly Inhomogeneous Electron Gas, *Solid St. Commun.* (in press.)



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Studies of Many-Body Effects in X-ray Spectroscopy of Solids.

1. Introduction

High-energy spectroscopy of solids is today one of the most important tools for the study of the electronic properties of solids. In these experiments one uses a deep core-level as a probe and studies transitions between this deep core-level and the valence states. In an emission experiment, where the empty core-state is filled by a valence electron, one obtains a map of the occupied part of the valence band, while the unoccupied part is sampled in absorption experiments. The classical experiments are soft X-ray emission and absorption where optical transitions between the valence band and one of the uppermost core-level are studied. The development started around 1930 with the pioneering work by Skinner, Siegbahn and Furineau and spectra showing Fermi edges, van Hove singularities and nearly free-electronlike bandwidths were observed. During the following period a large number of spectra was recorded, and the basic interpretation of the main bands and the additional structure due to e.g. doubly ionized core-levels was established.¹

Since the early works there has been a considerable improvement of the experimental technique, and today one has a large variety of experiments, such as inelastic scattering of X-rays or electrons, Auger spectroscopy which involves radiationless transitions to an unfilled core-level, and isochromat experiments where the X-ray yield is measured as a function of the excitation energy. These experimental investigations led to increased theoretical efforts and a deeper understanding of the problems. Still, however, many effects such as plasmon satellites in X-ray spectra, or the enhancement or depression of X-ray thresholds are only qualitatively understood.

The simplest model one can use for interpreting these experiments is the independent particle model, in which each individual particle is considered to move in the average field from all the remaining particles. Within this model the spectra have a direct and simple interpretation in terms of the number of one-particle states per unit energy. However, the spectra also show structure and satellites which cannot be explained within an independent particle model, but are due to the dynamical interaction between the electrons in the solid. Effects like plasmon satellites, edge enhancement and the influence of the initial excitation on the subsequent emission are completely outside the scope of one-body theory. Also less spectacular features like the valence bandwidth and the position of the core-levels can in principle only be obtained within the framework of many-body theory. The present thesis is devoted to a study of some of these effects.

Summary and discussion of papers.

A. In the ordinary treatment of X-ray or Auger emission the solid is considered to be in a fully relaxed "ground state" with one core-hole present before the emission takes place. This relaxed state has of course a small spread in energy, corresponding to the lifetime broadening of the core level. In the actual experiments, however, the core-hole is not created adiabatically, and "shake-up" excitations are always created along with the core-hole. These excitations can have many different forms, such as particle-hole pairs, plasmons or phonons. This is clearly seen in recent XPS experiments by Citrin², showing noticeable asymmetry of the main peak due to particle-hole excitations. For a core-hole with a long lifetime the initially created excitation will have time to leave the vicinity of the core-hole, and should not show up in the emission spectrum. If the lifetime of the core-hole is shorter, some of the excitations might still be close to the core-hole at the time of emission. These excitations will then have a possibility to interact with the outgoing particle and thus influence the emission spectrum. In this way a link between the initial excitation and the subsequent emission is established. To pursue these ideas further, one has to consider the excitation and the reemission as one quantum-mechanical process rather than two independent events. The simple golden rule expression is then of no use, and one has to resort to second order perturbation theory.

In paper A the theory is developed for the case of Auger emission. The terms in the Hamiltonian responsible for the decay of the core-hole, i. e. the Auger terms, are treated as a time-dependent perturbation,

and this leads to divergent results unless the lifetime broadening is taken into account in a similar fashion as in resonance fluorescence in the weak coupling limit. The formalism is applied to a solvable unperturbed Hamiltonian, describing core-electrons coupled to a plasmon field. It is shown explicitly that for long core-hole lifetimes the emission spectrum is the same as in the two-step approximation. The possibility of high-energy satellites in the case of short core-hole lifetimes is discussed. We suggest one should look for these effects in spectra from deeper core-levels with short lifetimes, e. g. in the KLL-spectra from Na and Al. A basic understanding of the incomplete relaxation in simple metals should be a good starting point for the analysis of more complicated systems such as e. g. the transition metals.

B. This paper is devoted to an accurate calculation of X-ray threshold energies, i. e. the energy of the fully relaxed state discussed in paper A. The core-hole is a very localized excitation, tightly bound to one of the nuclei. In metals the core-hole potential is completely screened outside the central Wigner-Seitz cell, and the position of the core-level should thus be quite insensitive to the symmetry of the lattice. In order to treat such localized excitations, a simple spherical model is developed. The lattice potential from the central nucleus is treated exactly, while the potential from the remaining sites is replaced by a spherical average of pseudo-ion potentials. Separate self-consistent calculations were made for the ground-state and the excited states involving one and two core-holes, and the threshold energies for both the main band and the satellite band due to double ionization were obtained from differences in total energies.

After an atomic correction obtained from the free ions had been added, the agreement with the experimental values was generally better than .5 eV, which confirms the basic assumptions made in paper B.

The phase shifts relevant to the Nozières-De Dominicis theory of X-ray edges are also calculated. We obtain a noticeable many-body enhancement of the $L_{2,3}$ edge in Na while the many-body effect in Li and Al is negligible. Our exponents do not agree with recent experimental results, and suggest a revision of the present form of the many-body theory of X-ray edges.

C. An investigation of the non-linear screening of a positive unit point charge in an electron gas at metallic densities is carried out by means of self-consistent Kohn-Sham ground state calculations. Large deviations from the linear screening results are found, especially for the induced charge density at the impurity. A remarkable result is that the screening length is almost independent of the density in the metallic regime. The Kohn-Sham ground state contains two bound electrons already at $r_s=2$, but the density seems to be continuous at the transition point. An error in an earlier work by Kohn and Majumdar on this subject is pointed out.

D. In this paper an analysis of the Hartree-Fock density response function is carried out in the long wave length limit. The calculation is made for an arbitrary interparticle interaction, and an exact expression for the first gradient correction to the exchange energy functional, which enters in the Kohn-Sham local density theory, is found. It is shown that the gradient correction

is divergent in the case of Coulomb interaction contrast to an earlier work by Sham. In view of these results, an application of Hartree-Fock electron-gas results with the aim to obtain quantitative inhomogeneity corrections for atoms, has no theoretical foundation.

Acknowledgements.

I feel much indebted to Professor Lars Hedin who brought me into the field of solid state physics and who has shown great interest in and given strong support to my scientific work.

To my collaborator Civ. ing. Ulf von Barth I also owe my sincere thanks for frequent and valuable discussions during several years.

I am grateful to Professor D.J.W. Geldart who was co-author of the fourth paper of this thesis.

I am grateful to Pavla Kruzela for typing the manuscript and to Civ. ing. Günter Grossman for critical reading the manuscript.

The Swedish Natural Science Research Council is thanked for financial support during the years 1972 - 1974.

Lund, 7 November 1974

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